National Park Service
U.S. Department of the Interior

Air Resources Division

Study Design for Ozone Passive Sampling

John D. Ray
NPS Air Resources Division

Exposure times – There is a balance to be made in the selecting the amount of time to expose the samplers. A certain amount of labor and lab analysis cost goes with each sampler. If sampling is too frequent, the cost of passive sampling becomes prohibitive. The other consideration is detection limits and performance linearity. The minimum detection limit is approximately 1.5 ppb for a week exposure and about 5 ppb for an exposure of 48 hours. An 8-hour exposure can be used, but at high uncertainty. The normal one-week exposure time is convenient as a return time and a comprise on resolution versus cost. Exposures beyond 2-3 weeks run into problems of non-linear response by the samplers.

Calibration - It is important to keep in mind that the passive ozone samplers have no inherent calibration. Although theorically a collection factor can be calculated, in practice there is variation in the effective collection rate and the collection factor must be determined empirically. Therefore, a least one collocated reference ozone monitor is recommended in the region where samples will be taken.

Blanks - The other important correction is for different batches of nitrite coatings and handling conditions for batches of the samplers. There is always some nitrate mixed in with the nitrite and more that forms from non-ozone reactions. Slow formation of nitrate has been observed in stored samples that are sealed in plastic bags and shipping vials. Temperature accelerates this process. To account for handle and batches, samples called “blanks” are shipped to the field and then returned to the lab unexposed. The nitrate mass on these blanks are taken as the baseline to be subtracted from all other samples from the same batch.

Duplicates - Duplicates serve several purposes: checks on lab procedures, estimates of precision, increased likelihood of getting a valid sample. Ideally, all samples would be run in triplicate, outliers discarded, and replicates averaged. That increases the cost a lot. A few duplicates each month gives a spot check on lab procedures, gives an estimated precision, and improves the data capture a little. When duplicates do not agree within the normal precision, then one or more of the samples may have to be invalidated and the problem identified.

Sampling design - The number of samplers needed for a program depends on the number of sites, blanks, and duplicates. The example below has 6 sites in 3 parks for a 16 week study that needs 127 samplers. The number of duplicates can be adjusted upward if desired. This pattern checks the precision at each park and has separate blanks for each park.

Table 1. Example pattern of number of samplers to use in parks with different numbers of sites.

			May				June				July					Aug			
	week of month ==>		1	2	3	4	1	2	3	4	1	2	3	4	5	1	2	3	4
Park	**# sites**	week of study ==>		**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
Park A	1	**Samples**		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
		Dupl		1			1				1					1			
		Blanks		1			1				1					2			
Park B	3	**Samples**		3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
		Dupl		1			1				1					1			
		Blanks		2			1				1					1			
Park C	2	**Samples**		2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
		Dupl		2			2				2					2			
		Blanks		2			1				1					1			

Known handling problems - Experience has shown that samplers mistreated by exposure to high temperature, sunlight, or left outside their plastic bags give erroneous values. If samplers get wet or the badges end up laying on the ground, them collection rates are different than the standard exposure and results can be much lower than the actual average ozone concentration. The most common cause of sample invalidation is failure to record full information on start, stop, and sample ID.

Calculation of the ozone concentration

The following equations are used for the weekly passive ozone samples:

$$\text{ppb-hrs} = [(\text{ug/mL}) * \text{Vol} * 6.572 \times 10^{3}] \ / \ R \qquad (1)$$

$$\text{Net ppb-hrs} = [\ \text{ppb-hrs}_{(\text{sample})} \ - \ \text{ppb-hrs}_{(\text{blanks})}\ ] \qquad (2)$$

$$C_{O3} \ = \ [\ \text{Net ppb-hrs} \ / \ \text{Time}\ ] \qquad (3)$$

where

C_{O3}	ozone mixing ratio, ppbv
Time	exposure time, hrs
R	collection factor, cm^3/min
Vol	extraction volume, mL
ug/mL	nitrate determined by lab analysis

An average collection factor (R) from field studies and comparison to reference analyzers was determined to be 32.0 cm^3/min. In the absence of a co-located reference analyzer, this factor should be used.

If data from co-located reference ozone analyzer is available, a mass of nitrate vs. average weekly ozone plot can be used to calculate ozone for passive samplers. The disadvantage of this method is the limited range of concentrations and data points being used for the calibration. It also ties the passives to a single ozone analyzer. Smaller passive sampling programs should use the average collection factor above and check results with co-located samples.

Additional information on the passive ozone monitoring

A fact sheet on passive ozone sampling, field standard operating procedures, reports, and articles can be found on the ARD web site at http://www2.nature.nps.gov/air/studies/passives.htm .